POTENTIAL USES FOR THE TIRE DERIVED PARTICLES PRODUCED BY THE WOMBAT PROCESS.*

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Approximately 275 million scrap tires are produced in the United States annually. Most of these tires are not being recycled. At best, they are an expensive nuisance. At worst, they cause significant air, water and soil pollution.

The typical modern tire is composed of a complex inert organic matrix into which several inorganic species have been impregnated to enhance the performance of the tire. Any potential uses of the scrap tires, other than simple (and expensive) reshaping of the physical appearance of the tires, must deal with these inorganic species and the C-C bonding network, both at the molecular level. The Wertz Oxidative Molecular Bombardment at Ambient Temperature (WOMBAT) process attacks the tires at this level. The final product of the WOMBAT process is referred to as tire-derived particles (TDP).

Shown in Figure 1A is the wavelength dispersive x-ray spectrum (WDXRS) of a scrap tire. The peaks in a WDXRS may be related to the presence of an element in the sample by a combination of Bragg's law and Moseley's law, i.e., $Z_J = 1 + \{n/[2 \cdot d_{mono} \cdot Q \cdot \sin\theta]\}$; where Z_J is the atomic number of element J, n is the order of the reflection, d_{mono} is the d-spacing of the crystal monochromator, and 2θ is the angle at which the peak P_J (caused by element J) appears in the x-ray spectrum of the sample. The K_β and K_α peaks for zinc (first, second, and third order reflections), the K_β and K_α peaks for calcium, and the K_α peak for sulfur are clearly discernible in the spectrum, along with the peaks from the exciting radiation -- chromium. Shown in Figure 1B is the WDXRS of TDP which has been produced by the WOMBAT solvent in the closed reactor, indicating that the zinc and sulfur originally contained in the tire have been reduced to < the lower limit of detection for each element in the TDP.

The intensities of the peaks due to different elements (eg. zinc and sulfur in this WDXRS) may not be directly compared to evaluate the relative abundances of these elements without extensive absorption-enhancement corrections being applied to the intensity of the K_α peak characteristic of each element. However, the peak intensity of the K_α and/or K_β peaks in the WDXRS of this sample and in subsequent samples may be used to estimate the change in abundance of that element in a series of samples of similar composition. These WDXRS analyses may be made at least semi-quantitative via comparison to a series of external standard curves containing the element(s) of interest dispersed into a matrix which is similar to that of the TDP. Studies to develop the appropriate absorption-enhancement corrections for zinc and sulfur in a high carbon matrix are on-going.

A two-step process for converting scrap tires to more useful material is being developed in our laboratory. This process involves the use of oxidizing solvent(s) at ambient conditions to separate the scrap tire into (a) steel belts, (b) polymeric cords, and (c) chunks of black solid which have irregular sizes and shapes. These chunks of black solid are the subject of part two of the WOMBAT process, which involves further reaction of the black solid with an oxidizing solvent. The result of process step two is a pulpy material which may be easily washed, dried, and ground into particles.

The partial compositions (measured by gas chromatography) of two samples of TDP and a sample of the rubbery part of an untreated tire are compared in Table I. This comparison shows that the WOMBAT process reduces the carbon, sulfur, and hydrogen abundances, while significantly increasing the oxygen abundance. The results also shown that the largest changes in the carbon and oxygen abundances occur when the process was carried out in an "open" container; i.e., where an infinite supply of atmospheric oxygen and of moisture were present. However, when the black chunks were subjected to the WOMBAT process in a closed system for a much shorter period of time, the resulting changes in the carbon and oxygen abundances were much reduced. Under these conditions, the resulting TDP is principally carbon (ca. 75%), but it also contains a considerable amount of oxygen (ca. 13%). Studies are currently underway to determine the effect of reaction parameters on the carbon/oxygen ratio produced in the TDP. The sulfur content of the TDP was reduced to 0.8%, while the nitrogen content was increased to 2.6%, when the chunks were reacted in the closed WOMBAT container. Studies are currently being conducted to determine the effect(s) of reaction time and other parameters on the sulfur and nitrogen abundances in the resultant TDP.

All of the results discussed below were obtained from the sample produced in the closed container (TDPA).

^{13}C NMR indicates the absence of aromatic carbons in the WOMBAT TDP.

After minimal grinding, the TDP range in diameter from 1-100 μm and have highly irregular surfaces.

The WOMBAT particles produce a high temperature ash which is 2.4% of the original weight of the TDP. The principal components of the ash are zinc, calcium, iron, and titanium, as shown in Figure 2.

The WOMBAT TDP has been evaluated as a fuel. Shown in Table II is its specific heat compared to that of other, more conventional, fuels as measured in our laboratory using conventional oxygen bomb calorimetry. Our analyses indicate that the specific heat of the WOMBAT TDP is considerably higher than that of bituminous coal. When combusted in our entrained flow thermal reactor at 850°C for an extended period, there is no measurable production of soot from the TDP.

The TDP may be mixed with materials of lesser fuel value to produce synthetic fuel blends. Shown in Figure 3 are the specific heats measured for a series of mixtures containing the TDP mixed with sawdust. The linear relationship between composition and heat content ($R^2 = 0.996$) indicates that such a mixture may be predesigned to produce a synthetic fuel blend of preselected specific heat. Combustion of such a mixture offers significantly reduced $SO_x(g)$ in the effluent gas and significantly less ash than produced by combustion of typical bituminous coals. Combustion of such a mixture also offers a useful method for utilizing, and thus not landfilling, two nuisance solid wastes -- scrap tires and sawdust.

Experiments with mixtures containing municipal garbage, wood shavings, and other low fuel content solids are on-going.

In addition, preliminary tests indicate that the TDP are capable of extracting some metal ions and some anions from water. Shown in Figure 4 is the WDXRS of a TDP which has been treated with a solution containing $CdCl_2$. New peaks indicating the presence of both Cd(II) and of Cl^- are easily discernible, indicating that the TDP has sequestered each from an aqueous solution. Experiments designed to evaluate and then exploit these capabilities of the TDP are ongoing.

Preliminary evaluation of the TDP as a component for inclusion in specialized polymeric matrices has recently been initiated.

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TABLE I. PARTIAL COMPOSITION OF THE TDP COMPARED TO THE COMPOSITION OF THE UNTREATED TIRE.

ELEMENT	SAMPLE TIRE	TDPA	TDPB
C	82.4%	76.3%	48.3%
H	7.8%	2.8%	4.6%
S	2.0%	0.8%	0.4%
N	0.5%	2.6%	3.8%
O	2.4%	13.5%	33.9%

A The process was conducted in the enclosed WOMBAT reactor for 72 hours.

B The process was conducted in a flask which was exposed to atmospheric conditions for 168 hours.

TABLE II. COMPARISON OF THE SPECIFIC HEAT OF THE TDP TO THE SPECIFIC HEAT OF OTHER FUELS USING OXYGEN BOMB CALORIMETRY.

FUEL	SPECIFIC HEAT (kJ/g)	FUEL	SPECIFIC HEAT (kJ/g)
bituminous coal	23	sawdust	18
sub-bituminous coal	21	wood chips	18
lignite	19	garbage	16
WOMBAT TDP	32		

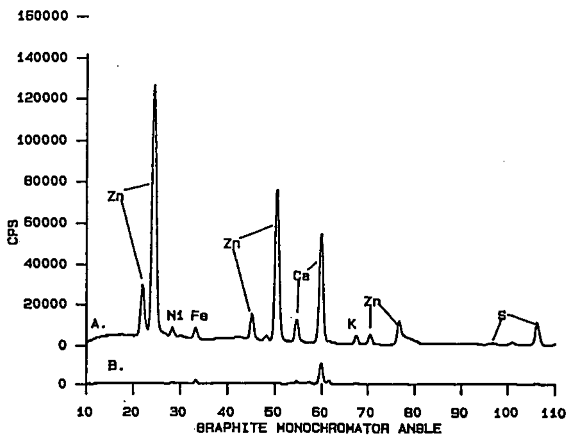

Figure 1. WDXRS of (A) a scrap tire, and (B) TDP produced from the tire.

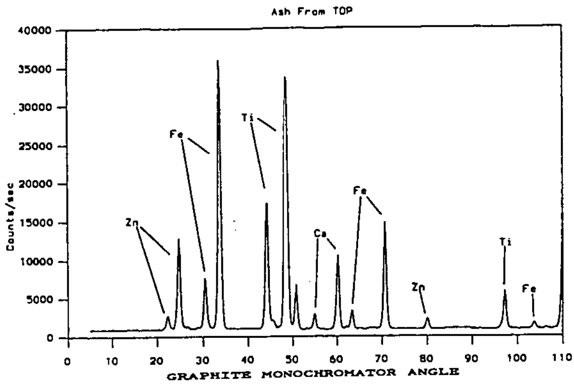

Figure 2. WDXRS of the high temperature ash produced from the TDP.

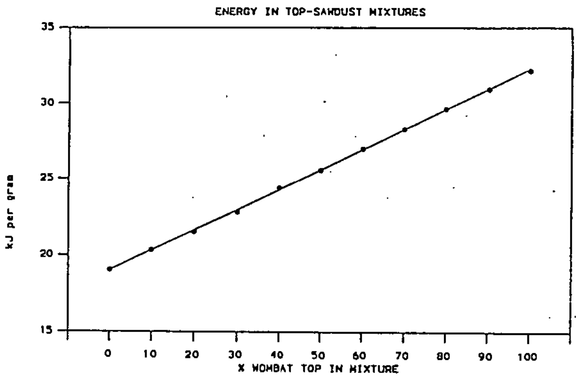

Figure 3. Specific heats of some TDP-sawdust mixtures.

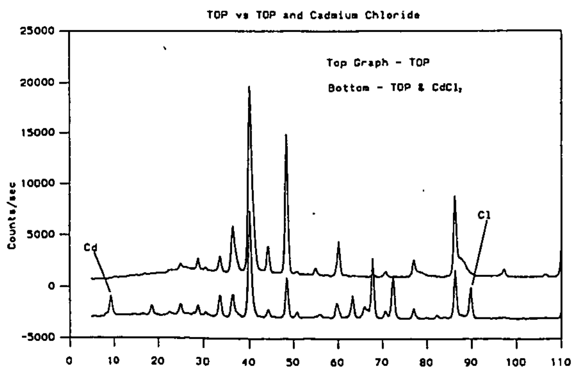

Figure 4. WDXRS of TDP treated with an aqueous solution of $CdCl_2$.